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(54) Title: PROCESS FOR THE POLYMERISATION OF ALPHA-OLEFINS

(57) Abstract

The present process for the preparation of polymers of alpha-olefins involves contacting, under effective polymerization conditions, at least one α-olefin having from 4 to 30 carbon atoms with a catalyst comprising a transition metal complex and a co-catalyst. The transition metal complex contemplated for use in the process consists of a reduced valency transition metal, selected from groups 4-6 of the Periodic Table of the Elements, with a multidentate monoanionic ligand and with two monoanionic ligands. In particular the reduced transition metal is titanium Ti^{+3}.

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PROCESS FOR THE POLYMERIZATION OF ALPHA-OLEFINS

BACKGROUND OF THE INVENTION

1. FIELD OF THE INVENTION

The present invention relates to the preparation of polymers of alpha-olefins. In particular the invention relates to a process for producing polymers of C_4-C_{30} α-olefins.

2. DESCRIPTION OF THE RELATED ART

In recent years α-olefin polymers of this type have received considerable attention as high performance functional fluids in a variety of applications.

WO-A-93/24539 discloses catalysts and processes to make low molecular weight, essentially terminally unsaturated, viscous poly(α-olefin) or copoly(α-olefin) using Group 4 metallocenes and an aluminoxane cocatalyst. The feed contains one or more C_3 to C_{20} α-olefin(s) and at least 1 wt.% isobutene. In a specific example poly(α-hexene) is obtained by contacting 1-hexene with a $(indenyl)_2ZrCl_2$/MAO system at 40° C for 20 hours. The resulting polymer has a Mn of 2653 g/mole. This catalyst has a very low polymerization activity.

With respect to this state of the art process, there is a need for a process which produces well-defined poly(α-olefin)s using a catalyst system which possesses high polymerization activity, in which the polymers have a narrow molecular weight distribution. There is a further need for such a process which is capable of producing such polymers having a narrow molecular weight distribution combined with a high temperature stability and the capability to

produce higher molecular weight polymers than with the process according to the state of the art at these higher temperatures, thus allowing for a more economical production process for poly(α-olefin)s.

U.S. Patent No. 5,364,994 describes the polymerization of olefinic hydrocarbons using a catalyst system comprising a tertiary organo halide and a Lewis acid catalyst. It is shown that a mixture of 1-octene and 1-dodecene can be polymerized to poly(α-olefin)polymers. In order to obtain reasonable molecular weights the polymerization is carried out at low temperatures of 5 - 10°C. GPC analysis of the polymers formed, using a polyisobutylene standard, indicates Mn = 4000 and Mw = 25000. For certain applications such a broad polymer molecular weight distribution can, however, negatively influence the performance.

EP-A-498 549 discloses the systhesis of α-olefin polymers, utilizing Ziegler-Natta polymerization. It is shown that terpolymers of C_{10}, C_{14} and C_{16} monomers can be prepared at 95°C with high molecular weight. All polymerizations result in terpolymers with a broad molecular weight distribution (MWD at least 7).

WO-A-94/13714 discloses the preparation of amorphous olefinic polymers, preferably poly-n-butenes, using cationic polymerization. The patent shows that at temperatures between -23°C and + 10°C low molecular weight compounds are produced (GPC : MW between 1600 and 3500). Only under specific conditions, higher molecular weight polymers are obtained at low temperature. In the latter case a multimodal distribution was always obtained.

EP-A-608 707 discloses the copolymerization of C_3 to C_{12} α-olefins with 0.01 to 5 mol% of ethylene, using metallocene catalysts. Polymerizations are

carried out at 80 - 100°C using the Cp_2ZrCl_2/methylaluminoxane catalyst system. Copolymers containing 2.8 mol% of ethylene have a molecular weight (Mw) of 4 kg/mol. When the same polymerization is carried out in the absence of ethylene the molecular weight is decreased by a factor of 3 and at the same time the polymerization activity diminished by a factor of 7.

EP-A-613 873 relates to a process for preparing liquid organic compounds, by contacting one or more α-olefins containing 8 to 20 carbon atoms per molecule with metallocene catalysts. The patent discloses the copolymerization of 1-octene with 1-dodecene at 30° C using a bis(cyclopentadienyl)zirconium dichloride/methyl-aluminoxane system. The poly(α-olefin) obtained had a maximum Mn of 650 g/mol.

SUMMARY AND OBJECTS OF THE INVENTION

It is therefore, an object of the present invention to solve the aforementioned problems associated with the related art as well as to address the need expressed above. In accordance with the principles of the present invention, this object is obtained by providing a process for the preparation of polymers of alpha-olefins and inparticular, the preparation of polymers and of copolymers C_4-C_{30} α-olefins.

Another object of the present invention is the provision of a polymer and particularly of polymers of C_4-C_{30} α-olefins by means of a polymerization process with utilization of the catalyst composition according to the invention.

The purpose of the present invention is to provide such a process, which also solves the problems

listed above for the state of the art processes, and which in particular can be used in a broad temperature range to produce polymers of greatly varying molecular weight and a narrow molecular weight distribution, and which can also provide poly(α-olefin)s which possess at least 30% terminal unsaturation, preferably at least 65% terminal unsaturation, most preferably at least 90% terminal unsaturation.

These terminally unsaturated poly(α-olefins) can be hydrogenated for improvement of their stability against oxidation, or can be functionalised, to obtain terminally functionalized well-defined poly(α-olefins).

The polymers according to the invention can be used as engine lubricants, hydraulic fluids, gear oils, lubricant additives, adhesives, glue and the like.

The process of the invention for the preparation of polymers of alpha-olefins comprises contacting, under effective polymerization conditions, at least one α-olefin having from 4 to 30 carbon atoms in the presence of the present catalyst composition.

The catalyst composition includes at least one complex comprising a reduced valency transition metal (M) selected from groups 4-6 of the Periodic Table of Elements, a multidentate monoanionic ligand (X), two monoanionic ligands (L), and, optionally, additional ligands (K). More specifically, the complex of the catalyst composition of the present invention is represented by the following formula (I):

$$\begin{array}{c} X \\ | \\ M - L_2 \\ | \\ K_m \end{array} \qquad (I)$$

wherein the symbols have the following meanings:

M a reduced transition metal selected from group 4, 5 or 6 of the Periodic Table of Elements;

X a multidentate monoanionic ligand represented by the formula: $(Ar-R_t-)_sY(-R_t-DR'_n)_q$;

Y a cyclopentadienyl, amido (-NR'-), or phosphido group (-PR'-), which is bonded to the reduced transition metal M;

R at least one member selected from the group consisting of (i) a connecting group between the Y group and the DR'_n group and (ii) a connecting group between the Y group and the Ar group, wherein when the ligand X contains more than one R group, the R groups can be identical to or different from each other;

D an electron-donating hetero atom selected from group 15 or 16 of the Periodic Table of Elements;

R' a substituent selected from the group consisting of a hydrogen, hydrocarbon radical and hetero atom-containing moiety, except that R' cannot be hydrogen when R' is directly bonded to the electron-donating hetero atom D, wherein when the multidentate monoanionic ligand X contains more than one substituent R', the substituents R' can be identical or different from each other;

Ar an electron-donating aryl group;

L a monoanionic ligand bonded to the reduced transition metal M, wherein the monoanionic ligand L is not a ligand comprising a cyclopentadienyl, amido (-NR'-), or phosphido (-PR'-) group, and wherein the monoanionic ligands L can be identical or different from each other;

K a neutral or anionic ligand bonded to the reduced transition metal M, wherein when the transition metal complex contains more than one ligand K, the ligands K can be identical or different from each

other;

m is the number of K ligands, wherein when the K ligand is an anionic ligand m is 0 for M^{3+}, m is 1 for M^{4+}, and m is 2 for M^{5+}, and when K is a neutral ligand m increases by one for each neutral K ligand;

n the number of the R' groups bonded to the electron-donating hetero atom D, wherein when D is selected from group 15 of the Periodic Table of Elements n is 2, and when D is selected from group 16 of the Periodic Table of Elements n is 1;

q,s q and s are the number of $(-R_t-DR'_n)$ groups and $(Ar-R_t-)$ groups bonded to group Y, respectively, wherein q + s is an integer not less than 1; and

t the number of R groups connecting each of (i) the Y and Ar groups and (ii) the Y and DR'_n groups, wherein t is selected independently as 0 or 1.

The objects, features, and advantages of the present invention will become apparent from the following detailed description when taken in conjunction with the accompanying drawings which illustrate, by way of example, the principles of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawings illustrate the present invention. In such drawings:

FIG. 1 is a schematic view of a cationic active site of a trivalent catalyst complex in accordance with an embodiment of the present invention; and

FIG. 2 is a schematic view of a neutral active site of a trivalent catalyst complex of a dianionic ligand of a conventional catalyst complex according to WO-A-93/19104.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Various components (groups) of the transition metal complex are discussed below in more detail.

(a) The Transition Metal (M)

The transition metal in the complex is selected from groups 4-6 of the Periodic Table of Elements. As referred to herein, all references to the Periodic Table of Elements mean the version set forth in the new IUPAC notation found on the inside of the cover of the Handbook of Chemistry and Physics, 70th edition, 1989/1990, the complete disclosure of which is incorporated herein by reference. More preferably, the transition metal is selected from group 4 of the Periodic Table of Elements, and most preferably is titanium (Ti).

The transition metal is present in reduced form in the complex, which means that the transition metal is in a reduced oxidation state. As referred to herein, "reduced oxidation state" means an oxidation state which is greater than zero but lower than the highest possible oxidation state of the metal (for example, the reduced oxidation state is at most M^{3+} for a transition metal of group 4, at most M^{4+} for a transition metal of group 5 and at most M^{5+} for a transition metal of group 6).

(b) The X Ligand

The X ligand is a multidentate monoanionic ligand represented by the formula: $(Ar-R_t-)_sY(-R_t-DR'_n)_q$.

As referred to herein, a multidentate monoanionic ligand is bonded with a covalent bond to the reduced transition metal (M) at one site (the anionic site, Y) and is bonded either (i) with a coordinate bond to the transition metal at one other

site (bidentate) or (ii) with a plurality of coordinate bonds at several other sites (tridentate, tetradentate, etc.). Such coordinate bonding can take place, for example, via the D heteroatom or Ar group(s). Examples of tridentate monoanionic ligands include, without limitation, $Y\text{-}R_t\text{-}DR'_{n-1}\text{-}R_t\text{-}DR'_n$ and $Y(\text{-}R\text{-}DR'_n)_2$. It is noted, however, that heteroatom(s) or aryl substituent(s) can be present on the Y group without coordinately bonding to the reduced transition metal M, so long as at least one coordinate bond is formed between an electron-donating group D or an electron donating Ar group and the reduced transition metal M.

R represents a connecting or bridging group between the DR'_n and Y, and/or between the electron-donating aryl (Ar) group and Y. Since R is optional, "t" can be zero. The R group is discussed below in paragraph (d) in more detail.

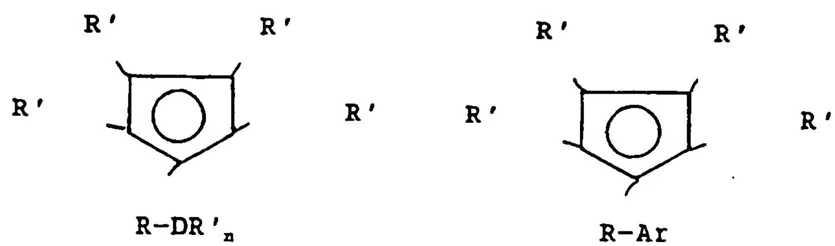
(c) The Y Group

The Y group of the multidentate monoanionic ligand (X) is preferably a cyclopentadienyl, amido (-NR'-), or phosphido (-PR'-) group.

Most preferably, the Y group is a cyclopentadienyl ligand (Cp group). As referred to herein, the term cyclopentadienyl group encompasses substituted cyclopentadienyl groups such as indenyl, fluorenyl, and benzoindenyl groups, and other polycyclic aromatics containing at least one 5-member dienyl ring, so long as at least one of the substituents of the Cp group is an $R_t\text{-}DR'_n$ group or $R_t\text{-}Ar$ group that replaces one of the hydrogens bonded to the five-member ring of the Cp group via an exocyclic substitution.

Examples of a multidentate monoanionic ligand with a Cp group as the Y group (or ligand) include the following (with the $(\text{-}R_t\text{-}DR'_n)$ or $(Ar\text{-}R_t\text{-})$ substituent

on the ring):



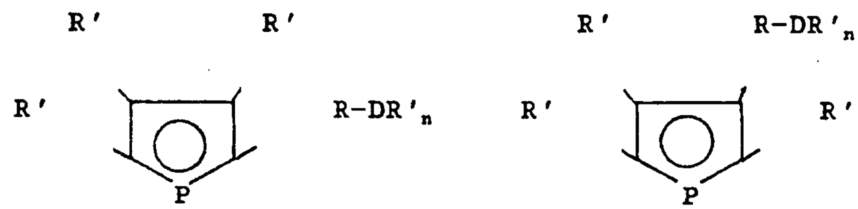
(II)

The Y group can also be a hetero cyclopentadienyl group. As referred to herein, a hetero cyclopentadienyl group means a hetero ligand derived from a cyclopentadienyl group, but in which at least one of the atoms defining the five-member ring structure of the cyclopentadienyl is replaced with a hetero atom via an endocyclic substitution. The hetero Cp group also includes at least one R_t-DR'$_n$ group or R_t-Ar group that replaces one of the hydrogens bonded to the five-member ring of the Cp group via an exocyclic substitution. As with the Cp group, as referred to herein the hetero Cp group encompasses indenyl, fluorenyl, and benzoindenyl groups, and other polycyclic aromatics containing at least one 5-member dienyl ring, so long as at least one of the substituents of the hetero Cp group is an R_t-DR'$_n$ group or R_t-Ar group that replaces one of the hydrogens bonded to the five-member ring of the hetero Cp group via an exocyclic substitution.

The hetero atom can be selected from group 14, 15 or 16 of the Periodic Table of Elements. If there is more than one hetero atom present in the five-member ring, these hetero atoms can be either the same or different from each other. More preferably, the hetero atom(s) is/are selected from group 15, and still more preferably the hetero atom(s) selected is/are

phosphorus.

By way of illustration and without limitation, representative hetero ligands of the X group that can be practiced in accordance with the present invention are hetero cyclopentadienyl groups having the following structures, in which the hetero cyclopentadienyl contains one phosphorus atom (i.e., the hetero atom) substituted in the five-member ring:



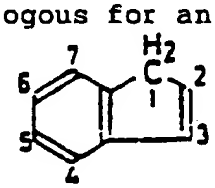
(III)

It is noted that, generally, the transition metal group M is bonded to the Cp group via an η^5 bond.

The other R' exocyclic substituents (shown in formula (III)) on the ring of the hetero Cp group can be of the same type as those present on the Cp group, as represented in formula (II). As in formula (II), at least one of the exocyclic substituents on the five-member ring of the hetero cyclopentadienyl group of formula (III) is the R_t-DR'$_n$ group or the R_t-Ar group.

The numeration of the substitution sites of the indenyl group is in general and in the present description based on the IUPAC Nomenclature of Organic Chemistry 1979, rule A 21.1. The numeration of the substituent sites for indene is shown below. This numeration is analogous for an indenyl group:

Indene



(IV)

The Y group can also be an amido (-NR'-) group or a phosphido (-PR'-) group. In these alternative embodiments, the Y group contains nitrogen (N) or phosphorus (P) and is bonded covalently to the transition metal M as well as to the (optional) R group of the ($-R_t-DR'_n$) or ($Ar-R_t-$) substituent.

(d) The R Group

The R group is optional, such that it can be absent from the X group. Where the R group is absent, the DR'_n or Ar group is bonded directly to the Y group (that is, the DR'_n or Ar group is bonded directly to the Cp, amido, or phosphido group). The presence or absence of an R group between each of the DR'_n groups and/or Ar groups is independent.

Where at least one of the R groups is present, each of the R group constitutes the connecting bond between, on the one hand the Y group, and on the other hand the DR'_n group or the Ar group. The presence and size of the R group determines the accessibility of the transition metal M relative to the DR'_n or Ar group, which gives the desired intramolecular coordination. If the R group (or bridge) is too short or absent, the donor may not coordinate well due to ring tension. The R groups are each selected independently, and can generally be, for example, a hydrocarbon group with 1-20 carbon atoms (e.g., alkylidene, arylidene, aryl alkylidene, etc.). Specific examples of such R groups include, without limitation, methylene, ethylene, propylene, butylene, phenylene, whether or not with a substituted side chain. Preferably, the R group has the following structure:

$$(-CR'_2-)_p \qquad (IV)$$

where p = 1-4. The R' groups of formula (IV) can each

be selected independently, and can be the same as the R' groups defined below in paragraph (g).

In addition to carbon, the main chain of the R group can also contain silicon or germanium. Examples of such R groups are: dialkyl silylene ($-SiR'_2-$), dialkyl germylene ($-GeR'_2-$), tetra-alkyl silylene ($-SiR'_2-SiR'_2-$), or tetraalkyl silaethylene ($-SiR'_2CR'_2-$). The alkyl groups in such a group preferably have 1-4 carbon atoms and more preferably are a methyl or ethyl group.

(e) The DR'_n Group

This donor group consists of an electron-donating hetero atom D, selected from group 15 or 16 of the Periodic Table of Elements, and one or more substituents R' bonded to D. The number (n) of R' groups is determined by the nature of the hetero atom D, insofar as n being 2 if D is selected from group 15 and n being 1 if D is selected from group 16. The R' substituents bonded to D can each be selected independently, and can be the same as the R' groups defined below in paragraph (g), with the exception that the R' substituent bonded to D cannot be hydrogen.

The hetero atom D is preferably selected from the group consisting of nitrogen (N), oxygen (O), phosphorus (P) and sulphur (S); more preferably, the hetero atom is nitrogen (N). Preferably, the R' group is an alkyl, more preferably an n-alkyl group having 1-20 carbon atoms, and most preferably an n-alkyl having 1-8 carbon atoms. It is further possible for two R' groups in the DR'_n group to be connected with each other to form a ring-shaped structure (so that the DR'_n group can be, for example, a pyrrolidinyl group). The DR'_n group can form coordinate bonds with the transition metal M.

(f) The Ar Group

The electron-donating group (or donor) selected can also be an aryl group ($C_6R'_5$), such as phenyl, tolyl, xylyl, mesityl, cumenyl, tetramethyl phenyl, pentamethyl phenyl, a polycyclic group such as triphenylmethane, etc. The electron-donating group D of formula (I) cannot, however, be a substituted Cp group, such as an indenyl, benzoindenyl, or fluorenyl group.

The coordination of this Ar group in relation to the transition metal M can vary from η^1 to η^6.

(g) The R' Group

The R' groups may each separately be hydrogen or a hydrocarbon radical with 1-20 carbon atoms (e.g. alkyl, aryl, aryl alkyl and the like as shown in Table 1).

Examples of alkyl groups are methyl, ethyl, propyl, butyl, hexyl and decyl. Examples of aryl groups are phenyl, mesityl, tolyl and cumenyl. Examples of aryl alkyl groups are benzyl, pentamethylbenzyl, xylyl, styryl and trityl. Examples of other R' groups are halides, such as chloride, bromide, fluoride and iodide, methoxy, ethoxy and phenoxy.

Also, two adjacent hydrocarbon radicals of the Y group can be connected with each other to define a ring system; therefore the Y group can be an indenyl, a fluorenyl or a benzoindenyl group. The indenyl, fluorenyl, and/or benzoindenyl can contain one or more R' groups as substituents. R' can also be a substituent which instead of or in addition to carbon and/or hydrogen can comprise one or more hetero atoms of groups 14-16 of the Periodic Table of Elements. Thus, a substituent can be, for example, a Si-containing group, such as $Si(CH_3)_3$.

(h) The L Group

The transition metal complex contains two monoanionic ligands L bonded to the transition metal M. Examples of the L group ligands, which can be identical or different, include, without limitation, the following: a hydrogen atom; a halogen atom; an alkyl, aryl or aryl alkyl group; an alkoxy or aryloxy group; a group comprising a hetero atom selected from group 15 or 16 of the Periodic Table of Elements, including, by way of example, (i) a sulphur compound, such as sulphite, sulphate, thiol, sulphonate, and thioalkyl, and (ii) a phosphorus compound, such as phosphite, and phosphate. The two L groups can also be connected with each other to form a dianionic bidentate ring system.

These and other ligands can be tested for their suitability by means of simple experiments by one skilled in the art.

Preferably, L is a halide and/or an alkyl or aryl group; more preferably, L is a Cl group and/or a C_1-C_4 alkyl or a benzyl group. The L group, however, cannot be a Cp, amido, or phosphido group. In other words, L cannot be one of the Y groups.

(i) The K Ligand

The K ligand is a neutral or anionic group bonded to the transition metal M. The K group is a neutral or anionic ligand bonded to M. When K is a neutral ligand K may be absent, but when K is monoanionic, the following holds for K_m:

$m = 0$ for M^{3+}

$m = 1$ for M^{4+}

$m = 2$ for M^{5+}

On the other hand, neutral K ligands, which by definition are not anionic, are not subject to the same rule. Therefore, for each neutral K ligand, the value of m (i.e., the number of total K ligands) is one higher than the value stated above for a complex having

all monoanionic K ligands.

The K ligand can be a ligand as described above for the L group or a Cp group ($-C_5R'_5$), an amido group ($-NR'_2$) or a phosphido group ($-PR'_2$). The K group can also be a neutral ligand such as an ether, an amine, a phosphine, a thioether, among others.

If two K groups are present, the two K groups can be connected with each other via an R group to form a bidentate ring system.

As can also be seen from formula (I), the X group of the complex contains a Y group to which are linked one or more donor groups (the Ar group(s) and/or DR'_n group(s)) via, optionally, an R group. The number of donor groups linked to the Y group is at least one and at most the number of substitution sites present on a Y group.

With reference, by way of example, to the structure according to formula (II), at least one substitution site on a Cp group is made by an R_t-Ar group or by an R_t-DR'_n group (in which case q + s = 1). If all the R' groups in formula (II) were R_t-Ar groups, R_t-DR'_n groups, or any combination thereof, the value of (q + s) would be 5.

One preferred embodiment of the catalyst composition according to the present invention comprises a transition metal complex in which a bidentate/monoanionic ligand is present and in which the reduced transition metal has been selected from group 4 of the Periodic Table of Elements and has an oxidation state of +3.

In this case, the catalyst composition according to the invention comprises a transition metal complex represented by formula (V):

$$\begin{array}{l} X \\ | \\ M(III) - L_2, \\ | \\ K_m \end{array} \qquad (V)$$

where the symbols have the same meaning as described above for formula (I) and where M(III) is a transition metal selected from group 4 of the Periodic Table of Elements and is in oxidation state 3+.

Such a transition metal complex has no anionic K ligands (for an anionic K, m = 0 in case of M^{3+}).

It should be pointed out that in WO-A-93/19104, transition metal complexes are described in which a group 4 transition metal in a reduced oxidation state (3+) is present. The complexes described in WO-A-93/19104 have the general formula:

$$Cp_a(ZY)_bML_c \qquad (VI)$$

The Y group in this formula (VI) is a hetero atom, such as phosphorus, oxygen, sulfur, or nitrogen bonded covalently to the transition metal M (see p. 2 of WO-A-93/19104). This means that the $Cp_a(ZY)_b$ group is of a dianionic nature, and has the anionic charges residing formerly on the Cp and Y groups. Accordingly, the $Cp_a(ZY)_b$ group of formula (VI) contains two covalent bonds: the first being between the 5-member ring of the Cp group and the transition metal M, and the second being between the Y group and the transition metal. By contrast, the X group in the complex according to the present invention is of a monoanionic nature, such that a covalent bond is present between the Y group (e.g., the Cp group) and transition metal, and a coordinate bond can be present between the transition metal M and one or more of the (Ar-R_t-) and (-R_t-DR$'_n$) groups. This changes the nature of the transition metal complex and

consequently the nature of the catalyst that is active in the polymerization. As referred to herein, a coordinate bond is a bond (e.g., H_3N-BH_3) which when broken, yields either (i) two species without net charge and without unpaired electrons (e.g., H_3N: and BH_3) or (ii) two species with net charge and with unpaired electrons (e.g., $H_3N^{\cdot +}$ and $BH_3^{\cdot -}$). On the other hand, as referred to herein, a covalent bond is a bond (e.g., CH_3-CH_3) which when broken yields either (i) two species without net charge and with unpaired electrons (e.g., $CH_3^{\cdot}$ and $CH_3^{\cdot}$) or (ii) two species with net charges and without unpaired electrons (e.g., CH_3^+ and $CH_3:^-$). A discussion of coordinate and covalent bonding is set forth in Haaland et al. (Angew. Chem Int. Ed. Eng. Vol. 28, 1989, p. 992), the complete disclosure of which is incorporated herein by reference.

The following explanation is proposed, although it is noted that the present invention is in no way limited to this theory.

Referring now more particularly to FIG. 2, the transition metal complexes described in WO-A-93/19104 are ionic after interaction with the co-catalyst. However, the transition metal complex according to WO-A-93/19104 that is active in the polymerization contains an overall neutral charge (on the basis of the assumption that the polymerizing transition metal complex comprises, a M(III) transition metal, one dianionic ligand and one growing monoanionic polymer chain (POL)). By contrast, as shown in FIG. 1, the polymerization active transition metal complex of the catalyst composition according to the present invention is of a cationic nature (on the basis of the assumption that the polymerizing transition metal complex - based on the formula (V) structure - comprises, a M(III) transition metal, one monoanionic bidentate ligand and one growing monoanionic polymer

chain (POL)).

Transition metal complexes in which the transition metal is in a reduced oxidation state, but have the following structure:

$$Cp - M(III) - L_2 \qquad (VII)$$

are generally not active in co-polymerization reactions. It is precisely the presence, in the transition metal complex of the present invention, of the DR'_n or Ar group (the donor), optionally bonded to the Y group by means of the R group, that gives a stable transition metal complex suitable for polymerization.

Such an intramolecular donor is to be preferred over an external (intermolecular) donor on account of the fact that the former shows a stronger and more stable coordination with the transition metal complex.

It will be appreciated that the catalyst system may also be formed in situ if the components thereof are added directly to the polymerization reactor system and a solvent or diluent, including liquid monomer, is used in said polymerization reactor.

The catalyst composition of the present invention also contains a co-catalyst. For example, the co-catalyst can be an organometallic compound. The metal of the organometallic compound can be selected from group 1, 2, 12 or 13 of the Periodic Table of Elements. Suitable metals include, for example and without limitation, sodium, lithium, zinc, magnesium, and aluminum, with aluminum being preferred. At least one hydrocarbon radical is bonded directly to the metal to provide a carbon-metal bond. The hydrocarbon group used in such compounds preferably contains 1-30, more preferably 1-10 carbon atoms. Examples of suitable

compounds include, without limitation, amyl sodium, butyl lithium, diethyl zinc, butyl magnesium chloride, and dibutyl magnesium. Preference is given to organoaluminium compounds, including, for example and without limitation, the following: trialkyl aluminum compounds, such as triethyl aluminum and tri-isobutyl aluminum; alkyl aluminum hydrides, such as di-isobutyl aluminum hydride; alkylalkoxy organoaluminium compounds; and halogen-containing organoaluminium compounds, such as diethyl aluminum chloride, diisobutyl aluminum chloride, and ethyl aluminum sesquichloride. Preferably, linear or cyclic aluminoxanes are selected as the organoaluminium compound.

In addition or as an alternative to the organometallic compounds as the co-catalyst, the catalyst composition of the present invention can include a compound which contains or yields in a reaction with the transition metal complex of the present invention a non-coordinating or poorly coordinating anion. Such compounds have been described for instance in EP-A-426,637, the complete disclosure of which is incorporated herein by reference. Such an anion is bonded sufficiently unstably such that it is replaced by an unsaturated monomer during the co-polymerization. Such compounds are also mentioned in EP-A-277,003 and EP-A-277,004, the complete disclosures of which are incorporated herein by reference. Such a compound preferably contains a triaryl borane or a tetraaryl borate or an aluminum equivalent thereof. Examples of suitable co-catalyst compounds include, without limitation, the following:

- dimethyl anilinium tetrakis (pentafluorophenyl) borate $[C_6H_5N(CH_3)_2H]^+ [B(C_6F_5)_4]^-$;
- dimethyl anilinium bis (7,8-dicarbaundecaborate)-cobaltate (III);

- tri(n-butyl)ammonium tetraphenyl borate;
- triphenylcarbenium tetrakis (pentafluorophenyl) borate;
- dimethylanilinium tetraphenyl borate;
- tris(pentafluorophenyl) borane; and
- tetrakis(pentafluorophenyl) borate.

If the above-mentioned non-coordinating or poorly coordinating anion is used, it is preferable for the transition metal complex to be alkylated (that is, the L group is an alkyl group). As described for instance in EP-A-500,944, the complete disclosure of which is incorporated herein by reference, the reaction product of a halogenated transition metal complex and an organometallic compound, such as for instance triethyl aluminum (TEA), can also be used.

The molar ratio of the co-catalyst relative to the transition metal complex, in case an organometallic compound is selected as the co-catalyst, usually is in a range of from about 1:1 to about 10,000:1, and preferably is in a range of from about 1:1 to about 2,500:1. If a compound containing or yielding a non-coordinating or poorly coordinating anion is selected as co-catalyst, the molar ratio usually is in a range of from about 1:100 to about 1,000:1, and preferably is in a range of from about 1:2 to about 250:1.

As a person skilled in the art would be aware, the transition metal complex as well as the co-catalyst can be present in the catalyst composition as a single component or as a mixture of several components. For instance, a mixture may be desired where there is a need to influence the molecular properties of the polymer, such as molecular weight and in particular molecular weight distribution.

In the process according to the invention, the polymerization of at least one α-olefin is carried

out using a catalyst composition as described above. In particular the α-olefin(s) is/are suitably chosen from α-olefins having from 4 to 30 carbon atoms, preferably α-olefins having from 8 to 20 carbon atoms, and most preferably α-olefins having from 8 to 18 carbon atoms. α-olefins with 8 to 20 carbon atoms per molecule are readily available from processes for the oligomerisation of ethylene according to the so called 'Aufbau"-principle. It may be feasible to select the ethylene-oligomerisation conditions such that mainly products within the desired range of 8 to 20 carbon atoms per molecule are formed. However, in most existing ethylene-oligomerisation processes, a wide range of olefins is formed, viz. olefins having from 4 to 30 carbon atoms per molecule. By conventional separation techniques, such as fractional distillation, olefins within the desired range of 8 to 20 and preferably within the range of 8 to 18 carbon atoms per molecule can easily be recovered.

A convenient process for the catalytic oligomerisation of ethylene is described in U.S. Patent No. 3,646,915, the complete disclosure of which is incorporated herein by reference.

In the process of the invention, alpha-olefins containing 8 to 20, and preferably 8 to 18 carbon atoms per molecule are polymerized to products, typically having a number-average molecular weight in the range of 400 to 3,000, preferably in the range of 400 to 1,000 and most preferably in the range of 400 to 700.

Products having higher molecular weights, e.g. number-average molecular weights of 3,000 or more, generally are less suitable as base materials for lubricants and hence the oligomerisation conditions are preferably selected such that the molecules of the obtained product are predominantly derived from 2 to 8

monomeric units. For certain applications, dimers are suitable which are, preferably, derived from monomers having carbon numbers in the higher region of the above mentioned carbon range. For certain other applications, however, products having a number-average molecular weight above 3000 g/mol can succesfully be applied.

Optionally, further α-olefin(s) may be used together with the C_4-C_{30} α-olefins mentioned above, in particular one or more selected from among ethylene, propylene and styrene (substituted or non-substituted), mixtures of which may also be used. More preferably, the α-olefin is ethylene, propylene or a mixture thereof. Mixtures of the above mentioned monomers can also be used.

According to this embodiment of the process of the invention, up to 60 mol% of the further α-olefin monomer(s) may be incorporated into the polymer and preferably up to 51 mol% (i.e. up to a slight excess of further α-olefinic monomer(s) with respect to the α-olefin monomer having 4 to 30 carbon atoms).

According to the present invention, the catalyst composition can be used supported as well as non-supported. The transition metal complex or the co-catalyst can be supported on a carrier. It is also possible that both the transition metal complex and the co-catalyst are supported on a carrier. The carrier material for the transition metal complex and for the co-catalyst can be the same material or a different material. It is also possible to support the transition metal complex and the co-catalyst on the same carrier. The supported catalyst systems of the invention can be prepared as setarate compounds, which can be used as such in polymerization reactions or the supported catalyst systems can be formed by in situ methods just before a polymerization reaction starts. The supported catalysts are used mainly in gas phase

and slurry processes. The carrier used may be any carrier known as carrier material for catalysts, for instance finely divided solid porous support, including, but not limited to $MgCl_2$, Zeolites, mineral clays, inorganic oxides such as talc, silica (SiO_2), alumina (Al_2O_3), silica-alumina, inorganic hydroxides, phosphates, sulphates, and the like, or resinous support materials such as polyolefins, including polystyrene, or mixtures thereof. The type or brand of carrier which is selectable is dependant on the structure of the metallocene. These carriers may be used as such or modified, for example by silanes and/or aluminium alkyles and/or aluminoxane compounds, etc.

Polymerization of the olefins can be effected in the gas phase, in the solid phase as well as in a liquid reaction medium. In the latter case, both solution and suspension polymerization are suitable. Also a very suitable polymerization method according to the present invention is polymerizing in bulk monomer (bulk polymerization) or mixture of monomers. The quantity of transition metal to be used in case of solution or suspension or bulk polymerization generally is such that its concentration in the dispersion agent amounts to 10^{-8} - 10^{-3} mol/l, preferably 10^{-7} - 10^{-4} mol/l.

The process according to the invention will hereafter be elucidated with reference to a preparation known per se of a polymer of α-olefins which is representative of the polymerization of the monomers meant here. The preparation of other polymers on the basis of α-olefinic monomers is the subject of numerous publications.

The preparation of polymers containing α-olefins by means of the catalyst compositions of the present invention is especially appropriate in solution, suspension (slurry) and bulk polymerization.

For a gas phase polymerization, no solvents or dispersion media are required. For solution or slurry polymerization processes, a solvent or a combination of solvents may be employed if desired. Suitable solvents include toluene, ethylbenzene, one or more saturated, straight or branched aliphatic hydrocarbons, such as butanes, pentanes, hexanes, heptanes, pentamethyl heptane or mineral oil fractions such as light or regular petrol, naphtha, kerosine or gas oil. For polymerization under slurry conditions, a suspension utilizing a perfluorinated hydrocarbon or similar liquid may in particular be used.

Also, excess olefinic monomer may be used as the reaction medium (so-called bulk polymerization processes).

Aromatic hydrocarbons, for instance benzene and toluene, as well as perfluorinated hydrocarbons can also be used, but because of their cost as well as on account of safety considerations, it will be preferred not to use such solvents for production on a commercial scale. In polymerization processes on a commercial scale it is preferred, therefore, to use low-priced solvent, such as aliphatic hydrocarbons or mixtures thereof, as marketed by the petrochemical industry. If an aliphatic hydrocarbon is used as solvent, the solvent may yet contain minor quantities of aromatic hydrocarbon, for instance toluene. Thus, if for instance methyl aluminoxane (MAO) is used as co-catalyst, toluene can be used as solvent for the MAO in order to supply the MAO in dissolved form to the polymerization reactor. Drying or purification is desirable if such solvents are used; this can be done without problems by the average person skilled in the art.

Gas-phase and slurry/suspension polymerizations are preferably carried out at

temperatures well below the melting temperature of the polymer produced, typically below 115°C. A solution or bulk polymerization is usually carried out at temperatures above the melting temperature of the polymers produced, typically above -100°C, preferably above 0°C, more preferably above 25°C and most preferably above 80°C.

The polymer solution or suspension resulting from the polymerization can be worked up by a method known per se. In general, the catalyst is de-activated at some point during the processing of the polymer. The de-activation is also effected in a manner known per se, e.g. by means of water or an alcohol. Removal of the catalyst residues can mostly be omitted because the quantity of catalyst in the polymer, in particular the content of halogen and transition metal is very low in the system according to the invention.

Polymerization can be effected at atmospheric pressure, at sub-atmospheric pressure, or at elevated pressure of up to 500 MPa, continuously or discontinuously. Preferably, the polymerization is performed at pressures between 1 kPa and 35 MPa. Higher pressures can be applied if the polymerization is carried out in so-called high-pressure reactors. In such a high-pressure process, the process according to the present invention can also be used with good results.

The polymerization can also be performed in several steps, in series as well as in parallel. If required, the catalyst composition, temperature, hydrogen concentration, pressure, residence time, etc. may be varied from step to step. In this way it is also possible to obtain products with a wide molecular weight distribution.

The invention also relates to the poly(α-olefin)s which can be obtained by means of the

polymerization process according to the invention.

The invention will now be elucidated by means of the following non-restrictive examples.

EXAMPLES

All tests in which organometallic compounds were involved were carried out in an inert nitrogen atmosphere, using standard Schlenk equipment. A method for synthesis of (dimethylaminoethyl)-tetramethyl cyclopentadienyl was published by P. Jutzi et al., Synthesis 1993, 684, the complete disclosure of which is incorporated herein by reference.

$TiCl_3$, the esters used and the lithium reagents, 2-bromo-2-butene and 1-chlorocyclohexene were obtained from Aldrich Chemical Company. $TiCl_3.3THF$ was obtained by heating $TiCl_3$ for 24 hours in THF with reflux. (THF stands for tetrahydrofurane). In the following 'Me' means 'methyl', 'iPr' means 'isopropyl, 'Bu' means 'butyl', 'iBu' means 'isobutyl', 'tertBu' means 'tertiary butyl' 'Ind' means 'indenyl', 'Flu' means 'fluorenyl', 'Ph' means 'phenyl'.

Pressures mentioned are absolute pressures.

Example I

This example concerns polymerization of octene using (dibutylaminoethyl)-tetramethylcyclopentadienyltitanium(III) dichloride ($C_5Me_4(CH_2)_2NBu_2TiCl_2$) as a catalyst.

Synthesis of the catalyst

a) Preparation of ethyl 3-(N,N-di-n-butylamino)propionate

Ethyl 3-bromopropionate (18.0 g; 0.10 mol) was added carefully to di-n-butylamine (25.8 g; 0.20 mol), followed by stirring for 2 hours. Then diethyl ether (200 ml) and pentane (200 ml) were added. The

precipitate was filtered off, the filtrate was evaporated and the residue was distilled at sub-atmospheric pressure. The yield was 7.0 g (31%).

b) Preparation of bis(2-butenyl)(di-n-butylaminoethyl)-methanol

2-Lithium-2-butene was prepared from 2-bromo-2-butene (16.5 g; 0.122 mol) and lithium (2.8 g; 0.4 mol) as in Example I. To this, the ester of a) (7.0 g; 0.031 mol) was added with reflux in approx. 5 minutes, followed by stirring for about 30 minutes. Then water (200 ml) was carefully added dropwise. The water layer was separated off and extracted twice with 50 ml of CH_2Cl_2. The combined organic layer was washed once with 50 ml of water, dried with K_2CO_3, filtered and evaporated. The yield was 9.0 g (100%).

c) Preparation of (di-n-butylaminoethyl)tetramethyl-cyclopentadiene)

4.5 g (0.015 mol) of the compound of b) was added dropwise to 40 ml of concentrated sulphuric acid of 0°C, followed by stirring for another 30 minutes at 0°C. Then the reaction mixture was poured out in a mixture of 400 ml of water and 200 ml of hexane. The mixture was made alkaline with NaOH (60 g) while being cooled in an ice bath. The water layer was separated off and extracted with hexane. The combined hexane layer was dried with K_2CO_3, filtered and evaporated. The residue was distilled at sub-atmospheric pressure. The yield was 2.3 g (55%).

d) Preparation of (di-n-butylaminoethyl)tetramethylcyclo-pentadienyltitanium(III)dichloride

1.0 equivalent of n-BuLi (0.75 ml; 1.6 M) was added (after cooling to -60°C) to a solution of the

$C_5Me_4H(CH_2)_2NBu_2$ of c) (0.332 g; 1.20 mmol) in THF (50 ml), after which the cooling bath was removed. After warming to room temperature, the solution was cooled to -100°C and then $TiCl_3.3THF$ (0.45 g; 1.20 mmol) was added in a single portion. After stirring for 2 hours at room temperature, the THF was removed at sub-atmospheric pressure.

e) Polymerization of octene

In a dry three neck vessel 25 ml toluene was added as a solvent, followed by 80 ml of dry octene, the addition of 0.011 mol triethylaluminium, 20 minutes of temperature equilibration at 120°C, the addition of 0.075 mol (Al-based) methylaluminoxane (Witco, 10% in toluene) and 4.2 x 10^{-5} mol of the reduced transition metal complex of Example I d) above. After 2 hours the polymerization was stopped by addition of methanol. The product was washed with 10% HCl in water, pure water, a saturated $NaHCO_3$ solution in water, finally followed by washing with pure water. The polymer was dried in a rotating evaporator (at 80°C and 10 mbar pressure). The polymer was found to have a number average molecular weight Mn of 896 and was found, with ^{1}H-NMR, to be mainly terminally unsaturated.

Example II

This example relates to the preparation of an octene / 1-octadecene copolymer using $Et(Cp(iPr)_3)NMe_2TiCl_2$ as a catalyst.

Synthesis of the $Et(Cp(iPr)_3)$ NMe_2TiCl_2 catalyst.

a) Reaction of cyclopentadiene with isopropyl bromide.

Aqueous KOH (50%; 1950g, ca. 31.5 mol in 2.483 l water) and ADOGEN 464® (phase transfer catalyst) (31.5g) were placed in a 3 l three-neck flask fitted with a

condenser, mechanical stirrer, heating mantle, thermometer, and an inlet adapter. Freshly cracked cyclopen-tadiene (55.3 g, 0.79 mol) and isopropyl bromide (364 g, 2.94 mol) were added and stirring was begun. The mixture turned brown and became warm (50°C). The mixture was stirred vigorously over night, after which the upper layer containing the product was removed. Water was added to this layer and the product was extracted with hexane. The combined hexane layer was washed once with water and once with brine, and after drying over $MgSO_4$), the solvent was evaporated, leaving a yellow-brown oil. GC and GC-MS analysis showed the product mixture to consist of diisopropyl-cyclopentadien (iPr_2-Cp, 40%) and triisopropylcyclopentadien (iPr_3-Cp, 60%). (iPr_2-Cp and iPr_3-Cp were isolated by distillation at reduced (20 mmHg) pressure. Yield depending on distillation accuracy was approx. 0.2 mol iPr_2-Cp (25%) and 0.3 mol iPr_3-Cp (40%).

<u>b) Reaction of lithium 1,2,4-triisopropylcyclopentadienyl with dimethylaminoethyl chloride.</u>

In a dry 500 ml flask under dry nitrogen, containing a magnetic stirrer, a solution of 62.5 ml of *n*-butyllithium (1.6 M in *n*-hexane; 100mmol) was added to a solution of 19.2 g (100 mmol) of iPr_3-Cp in 250 ml of THF at-60°C. The solution was allowed to warm to room temperature (in approx. 1 hour) after which the solution was stirred over night. After cooling to -60°C, dimethylaminoethyl chloride (11.3g, 105 mmol, freed from HCl by the method of Rees W.S. Jr. & Dippel K.A. in OPPI BRIEFS vol 24, No 5, 1992, the complete disclosure of which is incorporated herein by reference) was added via a dropping funnel in 5 minutes. The solution was allowed to warm to room

temperature after which it was stirred over night. The progress of the reaction was monitored by GC. After addition of water (and pet-ether), the organic layer was separated, dried and evaporated under reduced pressure. Next to the starting material iPr_3-Cp (30%), 5 isomers of the product (dimethylaminoethyl)triisopropylcyclopentadien (LH; 70%) are visible in GC. Two isomers are geminal (together 30%). Removal of the geminal isomers was feasible by precipitation of the potassium salt of the iPr_3-Cp anion and filtration and washing with pet-ether (3x). Overall yield (relative to iPr_3-Cp) was 30 mmol (30%).

<u>c) Reaction sequence to [1,2,4-triisopropyl-3-(dimethylaminoethyl)-cyclopentadenyl]titanium (III) dichloride.</u>

Solid $TiCl_3$3THF (18.53g, 50.0 mmol) was added to a solution of the potassium salt of iPr_3-Cp in 160 ml of THF at-60°C at once, after which the solution was allowed to warm to room temperature. The color changed from blue to green. After all the $TiCl_3$.3THF had disappeared the reaction mixture was cooled again to -60°C. After warming to room temperature again, the solution was stirred for an additional 30 minutes after which the THF was removed at reduced pressure.

<u>d) Polymerization</u>

In a 1.5 L stainless steel reactor 800 ml pentamethyl heptane (PMH) were introduced as a solvent. To the reactor were then dosed 0.013 mol triethylaluminium (TEA), 200 ml dry octene (C_8) and 38 ml dry 1-octadecene (C_{18}), respectively. The reactor was kept at a constant temperature of 298 K.
In a catalyst metering vessel of 100 ml, 25 ml PMH were introduced, followed by 0.09 mol (on Al-basis) of

methylaluminoxane (Witco, 10% in toluene) and 0.1 mmol of the reduced transition metal complex of Example II c). The resulting mixture was stirred for 1 minute. The polymerization reaction was started by introduction of the mixture from the catalyst metering vessel into the reactor. After one hour of polymerization, 25.2 grams of product were removed from the reactor. The copolymer molecular weight was determined to be : Mw = 2300 g/mol and Mn = 1000 g/mol.

Example III

This example concerns polymerization of 1-octene in the presence of ethylene using $EtCp*NMe_2TiCl_2$ as catalyst.

In a 1.5 L stainless steel reactor, 750 mL pentamethylheptane was introduced as the polymerization medium. In the next step 100 mL 1-octene was added. The temperature of the polymerization mixture was equilibrated at 50°C and the ethylene pressure was kept constant at 1.4 bar (140 kPa).
In a 100 mL catalyst premixing vessel 25 mL pentamethylheptane was added followed by 60 mL of a 10 wt.% solution of methylaluminoxane in toluene (Witco) and $5x10^{-5}$ mol of the reduced transition metal complex $EtCp^*NMe_2TiCl_2$. This mixture was mixed for 1 minute. The polymerization was started by the addition of this mixture from the catalyst premixing vessel into the reactor. After 30 minutes, the polymerization reaction was stopped, the polymer was drained from the reactor and was dried. The polymer yield was 19.9 grams. The polymer was analysed by SEC-DV using universal calibration. The Mw of the polymer was 270 kg/mol. The octene content in the polymer was 70 wt.%.

This example shows that the polymerization of higher olefins is also possible in the presence of a

lower olefin, such as ethylene, under effective polymerization conditions using the catalyst system of this invention.

Comparative Example 1

A polymerization was performed under the conditions described in Example I e) but with the addition of 0.011 mol triethylaluminium and $2.5x10^{-5}$ mol of the transition metal complex dimethyl-bis-(pentamethyl-cyclopentadienyl)zirconium.
The polymer formed was found to have a Mn of 224 g/mol. GC-MS measurements on the product showed that a large portion of the polymer formed, contained saturated chain ends which is uneconomical for functionalisation reactions.

Comparative Example 2

A polymerization was performed under the conditions described in Example I e) but with the addition of 0.011 mol triethylaluminium and $2.5x10^{-5}$ mol of the transition metal complex isopropylene-(9-fluorenyl)-cyclopentadienyl zirconium dichloride (prepared according to literature : J. Am. Chem. Soc. 110 (1988) 6255, the complete disclosure of which is incorporated herein by reference). The polymer formed had an average oligomerisation degree between 3 and 4.

A few non-limiting examples of transition metal complexes according to the invention are presented in Table 1.

Table 1 Examples of transition metal complexes according to the invention (see formulas I and V)

M	L	Y	R	D	R'	K
Ti	Cl	C_5H_4	dimethylsilyl	N	methyl	L
Zr	F	C_5Me_4	diethylsilyl	P	ethyl	Y-R'
Hf	Br	Indenyl	dipropylsilyl	As	propyl	X
V	I	Fluorenyl	dibutylsilyl	Sb	n-butyl	diethyl ether
Nb	methyl	benzofluorenyl	methylamido	O	n-pentyl	tetrahydrofuran
Ta	methoxy	octahydrofluorenyl	dimethylgermanyl	S	methoxy	trimethylamine
Cr	ethoxy	C_5H_3(N-Bu)	diethylgermanyl	Se	ethoxy	triethylamine
Mo	hydride	tetrahydroindenyl	diethylpropylene		Cl	trimethylphosphine
W	isopropyl	$C_5H_3(SiMe_3)$	tetramethyldisiloxane		F	triethylphosphine
	octyl	methylamido	diphenylsilyl		Br	triphenylphosphine
	propoxy	phenylphosphido	tetramethylsilaethylene		I	dimethylsulphide
	phenoxy		methylene		phenoxy	dimethylaniline
	benzyl		diethylmethylene		benzyl	
	methylthio		ethylene		H	
			dimethylethylene			
			ethylphosphido			
			phenylphosphido			

WHAT IS CLAIMED IS:

1. A process for the preparation of polymers of alpha-olefins comprising contacting, under effective polymerization conditions, at least one α-olefin having from 4 to 30 carbon atoms in the presence of a catalyst comprising a reduced transition metal complex and a co-catalyst, wherein said reduced transition metal complex has the following structure:

$$\begin{array}{l} X \\ | \\ M - L_2 \\ | \\ K_m \end{array}$$

wherein:

M is a reduced transition metal selected from group 4, 5 or 6 of the Periodic Table of the Elements;

X is a multidentate monoanionic ligand represented by the formula $(Ar-R_t-)_sY(-R_t-DR'_n)_q$;

Y is a member selected from the group consisting of a cyclopentadienyl, amido (-NR'-), and phosphido (-PR'-) group;

R is at least one member selected from the group consisting of (i) a connecting group between the Y group and the DR'_n group and (ii) a connecting group between the Y group and the Ar group, wherein when the ligand X contains more than one R group, the R groups can be identical as or different from each other;

D is an electron-donating hetero atom selected from group 15 or 16 of the Periodic Table of

Elements;

R' is a substituent selected from the group consisting of a hydrogen, hydrocarbon radical and hetero atom-containing moiety, except that R' cannot be hydrogen when R' is directly bonded to the electron-donating hetero atom D, wherein when the multidentate monoanionic ligand X contains more than one substituent R', the substituents R' can be identical or different from each other;

Ar is an electron-donating aryl group;

L is a monoanionic ligand bonded to the reduced transition metal M, wherein the monoanionic ligand L is not a ligand comprising a cyclopentadienyl, amido (-NR'-), or phosphido (-PR'-) group, and wherein the monoanionic ligands L can be identical or different from each other;

K is a neutral or anionic ligand bonded to the reduced transition metal M, wherein when the transition metal complex contains more than one ligand K, the ligands K can be identical or different from each other;

m is the number of K ligands, wherein when the K ligand is an anionic ligand m is 0 for M^{3+}, m is 1 for M^{4+}, and m is 2 for M^{5+}, and when K is a neutral ligand m increases by one for each neutral K ligand;

n is the number of the R' groups bonded to the electron-donating hetero atom D, wherein when D is selected from group 15 of the Periodic Table of Elements n is 2, and when D is selected from group 16 of the Periodic Table of Elements n is 1;

q and s are the number of $(-R_t-DR'_n)$ groups and $(Ar-R_t-)$ groups bonded to group Y,

respectively, wherein q + s is an integer not less than 1; and

t is the number of R groups connecting each of (i) the Y and Ar groups and (ii) the Y and DR'_n groups, wherein t is selected independently as 0 or 1.

2. A process according to claim 1, wherein the Y group is a cyclopentadienyl group.

3. A process according to claim 2, wherein the cyclopentadienyl group is an unsubstituted or substituted indenyl, benzoindenyl, or fluorenyl group.

4. A process according to claim 2, wherein said reduced transition metal complex has the following structure:

$$\begin{array}{l} Y\ -\ R\ -\ DR'_n \\ | \\ M(III)\ -\ L_2, \\ | \\ K_m \end{array}$$

wherein:

M(III) is a transition metal from group 4 of the Periodic Table of the Elements in oxidation state 3+.

5. A process according to claim 2, wherein said reduced transition metal is titanium.

6. A process according to claim 2, wherein said electron-donating hetero atom D is nitrogen.

7. A process according to claim 2, wherein the R' group in the DR'_n group is an n-alkyl group.

8. A process according to claim 2, wherein said R group has the following structure:

$$(-CR'_2-)_p,$$

wherein p is 1, 2, 3, or 4.

9. A process according to claim 2, wherein said monoanionic ligand L is selected from the group consisting of a halide, an alkyl group, and a benzyl group.

10. A process according to claim 2, wherein the Y group is a di-, tri- or tetraalkyl-cyclopentadienyl.

11. A process according to claim 2, wherein said co-catalyst comprises a linear or cyclic aluminoxane or a triaryl borane or tetraaryl borate.

12. A process according to claim 2, wherein at least one member selected from the group consisting of said reduced transition metal complex and said co-catalyst is supported on at least one carrier.

13. The process according to claim 1, wherein at least one α-olefin is chosen from α-olefins having from 8 to 20 carbon atoms.

14. The process according to claim 1, wherein at least one further α-olefin is chosen from the group consisting of ethylene, propylene and styrene substituted styrene and a mixture of any thereof.

15. The process of claim 1, wherein the transition metal complex and the co-catalyst are present as a single component or as a mixture of components in the catalyst composition.

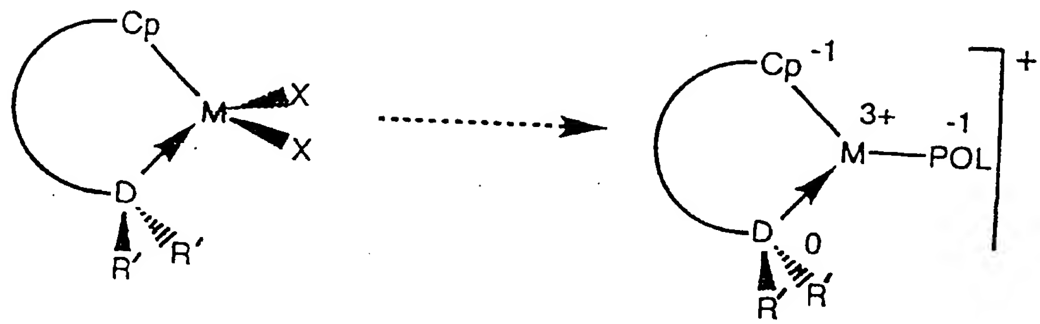


FIG. 1

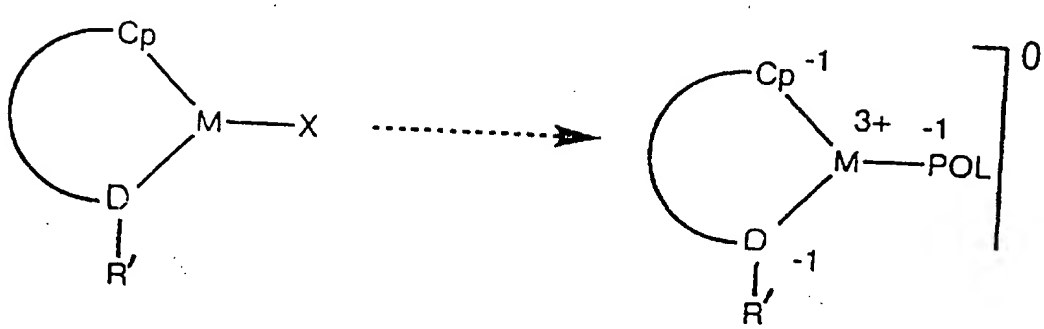


FIG. 2

INTERNATIONAL SEARCH REPORT

Intern. l Application No
PCT/NL 97/00248

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08F10/00 C08F4/64

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO 96 13529 A (DSM NV) 9 May 1996 * claims; page 13, lines 20 to 25; page 31, examples LV and LVI * ---	1-15
A	EP 0 416 815 A (DOW CHEMICAL CO) 13 March 1991 * claims 6-24, 30-36; page 5, lines 48-49; page 17, example 6 * ---	1-15
A	WO 93 08221 A (DOW CHEMICAL CO) 29 April 1993 * claims 9 and 19-27; page 31, lines 30-31 * ---	1-15
A	WO 93 19104 A (DOW CHEMICAL CO) 30 September 1993 cited in the application * claims; page 12, lines 31-32 * ---	1-15

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

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Date of the actual completion of the international search	Date of mailing of the international search report
3 June 1997	26.06.97

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Mergoni, M

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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